Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 630

Flocculation and Retention of Precipitated Calcium Carbonate by Cationic Polymeric Microparticle Flocculants

H. Ono and Y. Deng

December 1996

Submitted to
Journal of Colloid and Interface Science

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and

- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

FLOCCULATION AND RETENTION OF PRECIPITATED CALCIUM CARBONATE BY CATIONIC POLYMERIC MICROPARTICLE FLOCCULANTS

Hiroshi Ono[†] and Yulin Deng[*]

Institute of Paper Science and Technology

500 10th Street, N.W.

Atlanta, GA 30318

[†] : Present address: Central Research Laboratory, Nippon Paper Industries Co. Ltd., 5-21-1, Oji, Kita-ku, Tokyo 114, Japan.

[*]: To whom correspondence should be addressed.

ABSTRACT

A series of cationic polymeric microparticles (CPMP) with different charge densities and particle sizes were synthesized using emulsion or microemulsion polymerization. The interactions among positively charged polymeric microparticles, negatively charged fibers, and precipitated calcium carbonate (PCC) particles were studied. It has been found that although CPMP could adsorb onto a positively charged PCC particle surface, effective flocculation of PCC in water could not be obtained by CPMP alone. However, the combination of CPMP with an anionic polyacrylamide (APAM) did significantly improve the flocculation of PCC. The flocculation mechanics of PCC in this dual flocculation system was that the CPMP first created effective patches on the PCC surface, then APAM formed interparticle bridges through positively charged CPMP patches. It has also been found that the particle size and the surface charge of CPMP are two major factors affecting the flocculation of PCC suspension. The retention of PCC on wood fibers using a dual-flocculant system of CPMP-APAM was studied, and the related mechanism isdiscussed.

Key words: Cationic; polymer; microparticle; flocculation; retention.

INTRODUCTION

Cationic polyelectrolytes, including linear, graft, and crosslinked polymers, have been used extensively in papermaking as retention aids [1-7]. The bridging formation is the most common mechanism of fine and filler retention in papermaking. For an effective polymer bridging flocculation, (1) the polymer must be adsorbed onto the substrate surface, and (2) the loops of adsorbed polymer molecules must be long enough to overcome the repulsion force between particles. The former requires a high charge density of polyelectrolyte to generate a strong attractive force between polymer and particle, and the latter requires a low charge density of polyelectrolyte to form extended polymer loops. Both theoretical calculations [8] and experimental studies [9-11] indicated that high charged polymers adsorb in a flat rather than an extended conformation. This suggests that, as an effective bridging flocculant, the optimization of charge density and molecular weight is very important. However, this is sometimes difficult because most of the suspension systems are complicated and varied depending on the conditions. In addition to the polymer getting flat on a solid substrate, the penetration of water-soluble electrolytes into the pores of a solid surface may significantly affect both the dynamics and efficiency of bridging flocculation or patch formation. In contrast to a water-soluble polymer, the microparticle does not get flat on or penetrate into a porous particle because of its fixed structure. As a result, a more effective patch or bridge may be formed by a microparticle flocculant.

The fundamentals of particle bridging flocculation have been studied previously [12-15]. These studies clearly showed that the positively charged small polystyrene particles can strongly bond to the negatively charged large polystyrene latex, resulting in a particle bridging flocculation. Recently, Deng and Pelton [16,17] indicated that the microparticle bridging flocculation is more effective and less concentration-dependent compared to the neutralization flocculation caused by a water-soluble polyelectrolyte.

However, no information regarding the relationship between flocculation efficiency of the suspension and physical properties of microparticle bridges, such as microparticle size, surface charge density, and chemical composition, is available in the literature.

The interaction of cationic latex, mineral fillers, and paper sizing agents with wood fibers has been studied by Alince and co-workers [18-21]. A series of studies conducted by this group indicated that the deposition of clay, TiO_2, or latex particles proceeds in full agreement with the theoretical prediction of heterocoagulation of oppositely charged particles, but the deposition particles do not establish intimate contact with fibers. Although the interaction and deposition of cationic particles or latex have been studied, the application of cationic microparticles as a papermaking retention aid can be seen only in the patent works. Rushmere claimed [22] that the dual system containing a cationic colloidal silica sol and a high molecular weight cationic polymer is an effective retention and dewatering aid. Neff and Ryles [23] indicated that the cationic microparticles made by a crosslinked polyacrylamide can be used as a retention aid for papermaking. Although these primary works indicate that cationic microparticles can be an effective papermaking retention aid, the fundamentals and advantages of these retention systems over commercial anionic microparticle systems have not been addressed.

Anionic microparticle retention aids have been widely used in the papermaking industry since the early 1980s, and various mechanisms have been proposed [24-30]. These retention systems used an anionic microparticle in conjunction with a natural or synthetic polymer. Among these anionic microparticles, colloidal silica [29,31] and bentonite [32,33] are most commonly used in the paper industry. Polystyrene latex has also been studied in the literature [34]. A widely accepted model for anionic microparticle retention systems is that the cationic polymer patches are first formed on the surfaces of negatively charged fillers, fines, and fibers, then the anionic microparticles form bridges between suspended particles and fibers through pre-adsorbed cationic patches. The

conformation of pre-adsorbed polymer is important for a dual retention system, and the flocculation can be greatly enhanced by the manipulating polymer conformation [35,36]. As a model system, the microparticle has advantages over a water-soluble polymer for studying patch formation because there is almost no conformation change as a microparticle adsorbs onto an oppositely charged particle surface so that the patch thickness can be exactly controlled by the particle size. It is also expected that, from kinetics point of view, the patches formed by cationic microparticles are more effective than that formed by polyelectrolyte because the microparticles do not penetrate into the pores of solid surfaces.

Some advantages of using a cationic polymeric microparticle instead of an anionic microparticle as a papermaking retention aid have been demonstrated in our recent study. These advantages include very high retention efficiency compared to the normal cationic polyelectrolyte retention aid, enhancing the paper strength by adsorbing polymeric microparticles, improving paper sizing, cleaning white water, and reducing the total cationic demand in the papermaking process. The primary results regarding the application of cationic polymeric microparticles in papermaking will be published in a separate paper [37].

EXPERIMENTAL

Materials

Styrene (Aldrich Chem.) was distilled to remove inhibitors before use. Methacrylamidopropyl-trimethylammonium chloride (MAPTAC, 50% aqueous solution, Polysciences Inc.) was used as a cationic monomer to provide a positive charge for microparticles. Divinylbenzene (DVB, 55% solution, Aldrich Chem.) was used as a crosslinker. The cationic initiator, 2,2'-azobis(N,N'-dimethylene-isobutyramidine)dihydro-chloride (VA-044), was provided by Wako Pure Chemicals. Cationic surfactant,

cetyltrimethylammonium bromide (95%, Aldrich Chem.), was used as an emulsifier. The cationic monomer, crosslinker, initiator, and emulsifier were used as purchased.

Poly(diallyldimethylammonium chloride) (poly-DADMAC, Polysciences Inc., 15% solid) was used as a water-soluble cationic polyelectrolyte. The charge density of the polymer, determined by colloid titration, was 7.075 meq/g. The molecular weight of anionic polyacrylamide (APAM) (Polysciences Inc.) was 200,000 g/mol with a charge density of 11.1 meq/g.

Precipitated calcium carbonate (PCC) was a scalenohedral calcite filler product (Albacar HO®, Specialty Minerals Inc.) with an average particle size of 1.3 μm and specific surface area of 12 m^2/g.

Fibers used were once-dried bleached kraft softwood pulp. Clean fibers were prepared by three washes with deionized water followed by Büchner funnel filtration. The absence of water-soluble anionic polymers in pulp after washes was confirmed by colloid titration of the pulp supernatant.

Preparation of CPMP

The cationic polymeric microparticles with variable charge density and particle size were prepared using emulsion or microemulsion polymerization based on the method described by Goodwin and co-workers [38]. A typical example of polymerization (for sample C, see **Table I**) was given as follows. A double-wall glass reactor equipped with mechanical stirrer was filled with 150 ml of deionized water, 0.108 mol of styrene, 0.0043 mol of DVB, 0.0019 mol MAPTAC, and 0.0089 mol cationic surfactant. The solution was flashed with nitrogen for 30 minutes and thermostated at 60°C. After temperature equilibrium, 0.007 mol of VA-044 in 5 ml of deionized water was added. The polymerization was carried out under nitrogen at a stirring speed of 500 rpm for 4 hours.

The cationic polymeric microparticles were centrifuged twice (60,000 rpm, Beckman L-80 ultracentrifuge) for 120 minutes to remove cationic surfactant, excess monomers, and water-soluble polymers.

Physical property measurements

Flocculation: The flocculation of PCC suspension in water or in pulps was determined as follows. The PCC sludge was added into a 80-ml test tube and then diluted with water or pulp to 0.05 wt% consistency. The final volume of PCC suspension was adjusted to 50 ml using deionized water. The required amount of CPMP, poly-DADMAC, or APAM solution was added, and the mixture was immediately shaken for another few seconds. The mixture was allowed to stand for 10 minutes at room temperature. A 5-ml solution was carefully pipeted from the top, and the transmittance was measured using Shinazu UV160U spectra photometer at a wavelength of 550 nm. Deionized water was used as a reference (transmittance = 100%), and the suspension without adding any polymer was used as a control solution. The relative turbidity, τ/τ_0, was used to determine the flocculation ability of microparticles or polymers, where τ and τ_0 are the turbidities of the suspensions with and without flocculant (control solution), respectively.

Zeta potential: The electrophoretic mobility was measured using a Zetasizer 2c (Malvern) at a stationary position, and the zeta potential was calculated by computer using the Smoluchowski equation. The zeta potential of pulp fines was assumed to be representative of fibers.

Particle size: The particle size of cationic polymeric microparticles was determined by Doppler Electrophoretic Light Scattering (Zetasizer 2c, Malvern).

Adsorption isotherm: The adsorption of CPMP on PCC surfaces was measured at pH 9.3 and room temperature. The required CPMP and 0.25 g of PCC were mixed in 50

ml of water for 4 hours before analysis. The CPMP concentration of the supernatant was determined by the adsorbance at a wavelength of 550 nm using a concentration calibration of CPMP obtained by a Shinazu UV160U spectra photometer.

Retention: PCC retention on the fiber surface was investigated using a Dynamic Drainage Jar (DDJ) with a 200-mesh screen. A suspension containing 500 ml of pulp with a wood fiber consistency of 0.5% was added into the DDJ under a 1000 rpm stirring rate, then, the required polymer solution was followed. A solution containing 150 ml of first pass white water was collected after 45 seconds of the addition of the polymers. The first pass water from the DDJ was adjusted to a pH <3 by adding HCl at room temperature and standing for 10 minutes; then, an ~1-ml ammonia solution was added to the liquid bringing the pH to ~9.5. The calcium concentration was analyzed by potential titration using EDTA salt as a titrate. The end point of the titration was measured using a voltmeter, which was equipped with a calcium-selective electrode (Fisher product) and a glass pH reference electrode (Fisher product).

RESULTS

Microparticles

The properties of the microparticles prepared in this study are given in **Table I**. A typical example of the latex preparation and cleaning process has been given in the experimental section.

Generally speaking, both the size and electrostatic properties of the microparticles are a function of the concentrations of surfactant, crosslinker, cationic monomer, and temperature. It can be seen from **Table 1** that the surfactant concentration is the most important factor for particle size control. An increase in the particle size with an increase

in the cationic monomer content was also found, and this was attributed to the swelling of the microparticles.

Flocculation of PCC by CPMP alone

Because both PCC and CPMP are charged particles in water, the forces between these two particles strongly depend on the sign and the density of charges on both the particle surfaces. The dependence of zeta potential on pH for CPMP, PCC, and washed fibers (soluble and colloidal substances were washed out before zeta potential measurement) was investigated, and the results are shown in **Figure 1**. It can be seen that although the zeta potential decreases as pH is increased for all of the suspensions, only PCC has an isoelectric point (i.e.p.=10.5) in an interesting pH range. The zeta potential of PCC changing from positive to negative as pH increases is because of the decrease of Ca^{2+} concentration in the solution. The equilibrium concentration of calcium-containing species in calcium carbonate suspension has been extensively studied in the literature [39,40]. It was found [39] that the Ca^{2+} concentration decreases from 0.16 M to 1.0×10^{-7} M when the pH is increased from 7 to 10. The decrease in the Ca^{2+} concentration results in a reduction in Ca^{2+} adsorption and zeta potential of the PCC surface. In contrary to the PCC, the zeta potential of the CPMP (sample A) in water decreases slightly as the pH increases to 9.8, but drops sharply as pH further increases. The sharp decrease in the zeta potential is unlikely due to the hydrolysis or neutralization of the cationic repeat units, MAPTAC, because similar curves have been obtained for the cationic polymeric microparticles that were prepared in the absence of a cationic monomer. This suggests that the decrease in the zeta potential of CPMP with the increase of pH may be attributed to the hydrolysis of the polymer end groups, which were introduced by the cationic initiators during the polymerization.

The flocculation and the zeta potential of PCC suspension as a function of the concentration of CPMP are shown in **Figure 2**. It can be seen that the relative turbidity essentially remains almost a constant (from 1 to 1.15) as the concentration of CPMP is increased. The very small change in relative turbidity for this system indicates that CPMP alone is not an effective flocculant PCC in water. This is not surprising because both PCC and CPMP are positively charged in water so that the attractive force between CPMP and PCC is not strong.

It is interesting to note that, although the relative turbidity of the PCC suspension remains almost a constant, the zeta potential of the PCC suspension increases from 5 mV to 28 mV as the CPMP concentration increases from 0 to 40 mg/L. The increase of the zeta potential of PCC with an increase of CPMP concentration suggests that the CPMP can adsorb onto the PCC surface from water even though both of them are positively charged. It should be noted that, although the average zeta potential of the PCC particle is positive in this condition, the PCC surface is actually amphoteric because of the presence of CO_3^{2-} and Ca^{2+} ions. Therefore, the adsorption of positively charged CPMP on positively charged PCC should not be surprising. One of the other possible mechanisms may involve the exchange reaction between Ca^{2+} ions and CPMPs on the PCC surface. The adsorption of CPMP on the positively charged PCC was further confirmed by the adsorption isotherm (see below).

In contrary to the cationic polymeric microparticle, polyDADMAC (a linear cationic polymer) can flocculate the PCC in water at a certain concentration. **Figure 3** shows the relative turbidity of the PCC suspension as a function of poly-DADMAC concentration. It can be seen that the relative turbidity decreases sharply from 1 to 0.6 as the concentration of poly-DADMAC increases from 0 to 2 mg/L. Because there is no charge neutralization reaction between PCC and poly-DADMAC (both are positively charged), the flocculation at this low polymer concentration can be only attributed to the formation of an extended

poly-DADMAC bridge between PCC particles. When the concentration of poly-DADMAC is further increased, the relative turbidity increases to the same value as the reference. The increase of relative turbidity with the increase of poly-DADMAC concentration is the indication of the restabilization of PCC by adsorbed polyelectrolyte.

It is interesting to know how the electrostatic force between PCC and CPMP affects the flocculation. Because the surface charge of PCC is a function of the concentration of Ca^{2+} or CO_3^{2-}, it is convenient to modify the PCC surface charge by adding Ca^{2+} and CO_3^{2-} into the PCC suspension. **Figure 4** shows that the zeta potential of PCC changes as a function of Ca^{2+} and CO_3^{2-} concentration. Because the zeta potential of PCC is negative at a high concentration of sodium carbonate solution, it is expected that the attractive force between positively charged CPMP and negatively charged PCC is stronger than the attractive force between two positively charged particles as they are mixed in pure water. The strong attractive force may lead to an effective bridging formation and a significant flocculation of PCC suspension. This was confirmed by the turbidity measurements shown in **Figure 5**. It can be seen that in a 0.47-mM Na_2CO_3 solution, the relative turbidity of PCC sharply decreases then slightly increases as the concentration of CPMP is increased. It is clearly shown that the most effective flocculation (the lowest turbidity) was obtained when the zeta potential was close to i.e.p. Although the maximum flocculation at i.e.p. is commonly considered as an indication of neutralization coagulation rather than bridge flocculation, it is difficult to disguise these two mechanisms for this particular system because the microparticle has a rigid three-dimensional structure and it does not allow two PCC particles to attach to each other without the microparticle bridging. In other words, the neutralization flocculation caused by the cationic microparticle must involve a bridging formation between suspended particles. It should also be noted that the addition of CPMP is different from the addition of a normal electrolyte: the former does not significantly depress the thickness of the diffusion

electrical double layer of PCC due to the relatively large particle size (42.3 nm) of cationic microparticle size compared to polyelectrolyte, but the latter does. Although more work is needed to understand the relationship between particle bridging and charge neutralization, the results showed in **Figure 2** and **Figure 5** suggest that the formation of interparticle bridging by CPMP strongly depends on the surface charge of the PCC particles.

Flocculation of PCC by CPMP-APAM Dual-Flocculants

One of the important applications of PCC is to use it as a filler in papermaking. To obtain a good formation of paper products, the PCC must be uniformly distributed on the fiber surface. Because wood pulp contains many negatively charged materials, such as soluble and colloidal polymers and fibrils, the PCC is negatively charged in pulp. It is interesting to know if PCC can be flocculated by CPMP in the presence of negatively charged water-soluble polymers. As a model system, anionic polyacrylamide (APAM) was used as a water-soluble polymer in this study. In order to distinguish the effects between adsorbed and free anionic APAM on the flocculation of PCC, the APAM was added to the systems in different sequences. First, the PCC was pretreated by APAM adsorption, the free APAM was then washed out using deionized water, leaving only strongly bonded APAM on the PCC surface. These APAM-pretreated PCC particles showed a strong negative charge and they were a stable dispersion in water. The zeta potential and the relative turbidity of pretreated PCC suspension (0.05 wt%) as a function of CPMP concentration are shown in **Figure 6** (curve C). It can be seen that the relative turbidity of PCC in this system is significantly lower compared to that of unmodified PCC suspension **(Figure 2)**, which suggests that a flocculation of APAM-pretreated PCC was induced by flocculant of CPMP. Visual observation indicated that the flocculation of this system was fast and the flocs were larger than unmodified PCC. Because all of the free APAM had been removed from the solution (confirmed by colloidal titration) before

adding cationic polymeric microparticles, and the suspension of APAM-pretreated PCC was relatively stable in the absence of CPMP, the flocculation could not be attributed to the APAM alone, but was solely attributed to the bridging formation through a positively charged CPMP and PCC-bonded APAM.

The mechanism of flocculation of PCC in this system is further studied by changing the polymer addition sequence, i.e., by adding CPMP first followed by APAM. The relative turbidity obtained for this system is shown in **Figure 6** (curve D). It is interesting to note that the sequence of polymer addition can significantly affect the flocculation efficiency of PCC, and more effective flocculation was obtained by adding CPMP first followed by APAM. We believe that the different addition sequence will lead to different flocculation mechanisms. This will be further discussed below.

The Effect of Fibers on PCC Flocculation

It is well-known that commercial fibers contain soluble anionic materials such as fatty acids, low molecular weight lignin, and soluble wood materials, and these anionic polymers will adsorb onto fibers, fines, and fillers. In order to evaluate the interactions among PCC, CPMP, and fibers, the flocculation of PCC by CPMP in a clean bleached softwood kraft fiber furnish (extensively washed with deionized water) was compared with that in an original fiber furnish.

The experiments indicated that the zeta potential of both washed and unwashed fibers (assuming to be the same as fines) are strong negative in all of the pH range. However, the zeta potential of PCC suspension is different: it is negative in unwashed pulp but positive in washed pulp because of the presence and absence of anionic trash in these two pulps. **Figure 7** shows the relative turbidity of PCC suspension in these two pulps as a function of CPMP concentration. It can be seen that the clean fibers have little effect on the flocculation of PCC (where the relative turbidity is almost equal to one), but anionic

trash in unwashed pulp significantly enhanced the flocculation of PCC when CPMP flocculant was used. Although the presence of fibers can provide more surface area for the deposition of positively charged PCC, the flocculation measurement in a washed pulp suggests that the direct deposition of PCC is not significant. The difference between PCC flocculation in washed and unwashed pulps strongly suggests that the anionic trash in wood pulp plays an important role in bridging flocculation using CPMP as a flocculant.

Particle Size Effect

It has been found in the literature [24,28,34] that the size of an anionic microparticle retention aid is one of the most critical factors affecting the filler and fine retention on the wood fiber web: the smaller the microparticle size, the higher the retention efficiency. A similar conclusion was found in this study for our cationic polymeric microparticles. The first pass retention of PCC on the unwashed wood fiber web obtained by Dynamic Drainage Jar measurement is shown in **Figure 8**. It can be seen that the retention was not enhanced by the addition of a CPMP with a diameter of 364 nm, but was increased from 24% (without CPMP) to 56% by a CPMP with a diameter of 54 nm. The similar effect had been observed in our turbidity measurements. More details regarding the CPMP particle size effect on the PCC retention will be given in a separate paper [37].

Adsorption Isotherm

The adsorption isotherms of CPMP on PCC were measured, and the results are shown in **Figure 9**. It can be seen that the adsorption of CPMP on a negatively charged PCC (PCC a in 0.5-M Na_2CO_3 solution or APAM-pretreated PCC in water) is higher than that on a positively charged PCC (PCC in deionized water). This is consistent with the results obtained in flocculation measurements. It can also be seen that, for a positively charged PCC, the adsorption isotherm follows a Langmuir monolayer adsorption curve. As the equilibrium concentration of CPMP increases to 200 mg/L, the adsorption amount

of CPMP reaches a constant value. However, the adsorption of CPMP on the negatively charged PCC surfaces, such as APAM-pretreated PCC and PCC dispersed in a Na_2CO_3 solution, continually increases as the CPMP concentration is increased.

The fractional coverage θ_A of CPMP on the PCC surface can be calculated by adsorption amount using the following equation:

$$\theta_A = \frac{n\pi r^2}{S_A} = \frac{\frac{\Gamma}{v\rho}\pi r^2}{S_A} = \frac{3\Gamma}{4r\rho S_A} \qquad (1)$$

Where n is the number of CPMP on the surface of per gram PCC; r is the radius of microparticle (21.15×10^{-9} m for the sample used in the experiments); S_A is the specific surface area of PCC (m^2/g); Γ is the adsorption amount of CPMP on the PCC surface (g/g); V is the hydrodynamic volume of one CPMP (m^3); and ρ is the density of CPMP (assuming the density equals that of polystyrene, 1.1×10^6 g/m^3).

It should be noted that, as an accurate calculation, the hydrodynamic specific area should be used rather than the area obtained from BET adsorption because the CPMPs are hard spherical particles that cannot penetrate into the small pores of the PCC surface. However, according to the manufacturer, the PCC (Albacar HO®) can be treated as a nonporous particle. As an approximation, the specific surface area (12 m^2/g) obtained from BET adsorption is used as a hydrodynamic surface area in this calculation.

Substituting the data into equation (1), a fractional coverage, θ_A, of 10.5% was obtained for the positively charged PCC at saturated adsorption (39 mg/g). However, for the negatively charged PCC, such as PCC dispersed in a Na_2CO_3 solution or APAM-pretreated PCC in water, the fractional surface coverage was increased to 15-16% at the equilibrium CPMP concentration of 550 mg/L (no clear saturated adsorption was observed in these systems).

The zeta potential of PCC as a function of equilibrium CPMP concentration is shown in **Figure 10**. It is interesting that, for APAM-pretreated PCC in water and untreated PCC in a Na_2CO_3 solution, although the adsorption amount continually increases (see **Figure 8**), the zeta potential finally reaches a constant as the CPMP concentration increases. It has also been noted that the maximum zeta potential is as high as 28.9 mV for the PCC in water and in Na_2CO_3, respectively, but is only 13.4 mV for APAM-pretreated PCC. The lower zeta potential for APAM-pretreated PCC may result from the presence of nonreacted negative segments of APAM on the PCC surface.

Retention of PCC on Fiber Web by CPMP

The conclusions from turbidity measurements were further examined by retention test using CPMP as a retention aid in the presence and absence of APAM. The retention tests were carried out using a Dynamic Drainage Jar.

Figure 11 shows the retention of APAM-pretreated PCC on washed fibers (no anionic trash in the pulp) as a function of CPMP concentration. It can be seen that both the retention efficiency and the zeta potential increase as CPMP concentration increases. Because both fibers and APAM-pretreated PCC were negatively charged and there was no free anionic trash in the suspension, the retention could be only attributed to the bridging formation between adsorbed APAM and positively charged CPMP patches. This agrees well with the results obtained in the turbidity measurements.

Figure 12 shows the retention of APAM-pretreated PCC on washed fibers as a function of APAM in the presence of 40 mg/L CPMP. A sharp decrease in both the retention efficiency and zeta potential was observed as free APAM concentration initially increased from 0 to 4 mg/L. This could be attributed to the neutralization of CPMP by APAM, resulting in a weakening in the bonding strength between CPMP and APAM-

pretreated PCC. However, as the free APAM concentration increased further, the zeta potential of suspension decreased, but the retention efficiency of APAM-pretreated PCC sharply increased. We believe the increase in retention efficiency at high APAM concentration is attributed to the polymer-bridging formation of APAM rather than CPMP. In other words, the flocculation at high APAM concentration is dominated by polymer rather than microparticle bridging.

DISCUSSIONS

The Mechanism of PCC Flocculation Using CPMP

It has been shown in **Figure 6** that, as CPMP is used alone, both the sign and the density of the surface charge of PCC are important factors affecting the flocculation efficiency. It has also been shown that the addition of APAM will significantly enhance the flocculation of PCC in the presence of CPMP, but the addition sequence of anionic polymer and cationic microparticle is important. According to these experimental results, the possible flocculation mechanisms are suggested and schematically shown in **Figures 13-A** to **13-D**.

Figure 13-A shows the interaction between CPMP and PCC particles in water (corresponding to curve A in **Figure 6**). Because both the PCC and CPMP are positively charged, the repulsion force between two PCC particles is strong enough to prevent the approach of the particles. In this case, the bridging flocculation is almost ineffective.

Figure 13-B shows the interaction between PCC and CPMP in a sodium carbonate solution (corresponding to curve B in **Figure 6**). Since PCC is negatively charged in this solution, the attractive force between PCC and CPMP is relatively strong. As a result, the CPMP adsorbs more effectively onto the PCC surface (see adsorption isotherms in **Figure**

9) to form effective bridges between PCC and CPMP particles, which leads to an increase in flotation efficiency.

Figure 13-C shows the bridging formation in an APAM-CPMP dual-flocculant system where PCC was first modified by APAM (corresponding to curve C in **Figure 6**). It can be seen that the adsorbed APAM plays two roles: modifying the surface charge of PCC and forming a bridge with CPMP. Because the length of the bridge is increased compared to the bridge length formed by a single CPMP particle, a smaller repulsion force between bridged PCC particles and a more effective flocculation are expected in this dual-flocculant system than in a single CPMP flocculant system.

Figure 13-D shows two possible mechanisms for the bridge formation in a CPMP-APAM system where the CPMP was added before APAM (corresponding to curve D in **Figure 6**). Because the flocculation of PCC caused by single APAM (M_w = 200,000 g/mol) is not significant as tested in this study, and the results clearly show that the flocculation is not only a function of APAM but also a function of CPMP concentration, it is believed that the flocculation of PCC in this system is dominated by the bridging formation of both APAM and CPMP rather than any individual flocculant. As showed in **Figure 13-D**, tow possible mechanisms may be involved in this system. Because two components are involved in one bridge, the bridge length is longer than any single system, which results in a more effective flocculation.

All suggested mechanisms shown in **Figures 13-A** to **13-D** are consistent with the experimental results of **Figure 6**. Although more studies are needed to conduct the detail structures in those systems, the results obtained in this study clearly show that the flocculation strongly depends on the surface charge of PCC, the presence of soluble polyelectrolytes, and the bridge length.

Patch Formation

As discussed above, the effective flocculation of PCC in the dual-flocculant system of CPMP and APAM is through the bridge formation. The most effective bridge exists when the CPMP first adsorbs onto the PCC surface to form "patches," followed by the adsorption of APAM onto these cationic microparticle "patches." **Figure 14** shows the difference between the patches of cationic microparticles and water-soluble polyelectrolytes. The main differences between these two types of patches are (1) the thickness of the "microparticle patches" is greater than the "polymer patches" because of the flat conformation of the latter on the PCC surfaces, (2) the charge neutralization can only happen at immediately attached surfaces between CPMP and PCC, and the rest of the surface of CPMP can still remain a high positive charge. However, the most of the charges in the backbone of the soluble polyelectrolyte are neutralized by negative charges on the PCC surface because the positively charged repeat units in polymer chains are directly bound on the PCC surface; and (3) the effectiveness of a polymer patch may change with time because of the penetration of flexible polymer chains into the pores of a solid surface, but the "microparticle patch" is less time dependent.

CONCLUSIONS

Cationic polymeric microparticles with a broad surface charge and particle size can be synthesized using emulsion and microemulsion polymerization techniques. The surface charge of the microparticle is positive up to pH 11. These cationic polymeric microparticles can adsorb onto the PCC surface in water at an alkaline pH, but the adsorption is not strong. The CPMP is not an effective flocculant for positively charged PCC if it is used alone. However, the flocculation efficiency will be improved if the PCC surface is modified to negatively charged. The presence of a water-soluble anionic polymer will significantly affect the flocculation of PCC in the presence of CPMP.

Varying the polymer addition sequence will lead to different flocculation mechanisms, which may significantly affect the flocculation efficiency. Four different bridging mechanisms were proposed based on the experimental results obtained in this study.

ACKNOWLEDGMENT

The authors wish to thank Nippon Paper Industries Co. Ltd. for providing financial support for Mr. H. Ono's research at the Institute of Paper Science and Technology.

REFERENCES

1. Eklund, D., and Lindström, T., "Paper Chemistry," DT Paper Sci. Publ., Finland, 1991.
2. Lafuma, F., Wang, T., Durand, G., and Audebert, R., *Colloids Surface*, **31**, 255 (1988).
3. Wang, T., and Audebert, R., *J. Colloid Interface Sci.*, **119**, 459 (1987).
4. Gregory, J., *J. Colloid Interface Sci.*, **42**, 448 (1973).
5. Gregory, J., *J. Colloid Interface Sci.*, **55**, 35 (1976).
6. Tanaka, H., Ödberg, L., Wagberg L., and Lindström, T., *J. Colloid Interface Sci.*, **134,** 219 (1990).
7. Falk, M., Ödberg, L., Wagberg, L., and Risinger, G., *Colloids Surface*, **40**, 115 (1989).
8. Lyklema J., and Fleer, G., *Colloids Surface*, **25**, 357 (1987).
9. Ruehrwein, R., and Ward, D., *Soil Sci.*, **73**, 485 (1952).
10. Michaels, A., *Ind. Eng. Chem.* **46**, 1485 (1954).
11. Healy, T., and Lamer, V., *J. Phys. Chem.*, **66**, 1835 (1962).

12. Vincent, B., Young, C., and Tadros, T., *J. Chem. Soc. Faraday I*, **76**, 665 (1980).

13. Vincent, B., Jafelicci, M., Luckham, P., and Tadros, T., *J. Chem. Soc. Faraday I*, **76**, 674 (1980).

14. Luckham, P., Vincent, B., Hart, C., and Tadros, T., *Colloids Surfaces*, **1**, 281 (1980).

15. Luckham, P., Vincent, B., McMohan, J. and Tadros, T., *Colloids Surfaces*, **6**, 85 (1983).

16. Deng, Y., and Pelton, R., *Macromolecules*, **28**, 4617 (1995).

17. Deng, Y., Xiao, H., and Pelton, R., *J. Colloid & Interface Sci.*, **179**, 188 (1996).

18. Alince, B., *Colloids Surfaces*, **39**, 39 (1989).

19. Alince, B., Inoue M., and Robertson, A., *J. Appl. Polymer Sci.*, **20**, 2209 (1976).

20. Alince, B., and Van de Ven, T., *Colloids Surfaces A: Physicochemical Eng. Aspects*, **71**, 105 (1993).

21. Inoue, M., Alince, B., Shao, Y., and Van de Ven, T., *Proceedings* of *1996 International Paper and Coating Chemistry Symposium* 119 (1996).

22. Rushmere, J., U.S. Patent 4,798,653.

23. Neff, R., and Ryles, R., U.S. Patent 5,340,865.

24. Gill, R., *Paper Technology*, **32**, (8), 34 (1991).

25. Åsell, I., Björklund, M., Swerin A., and Wägberg, L., *Tappi J.*, **79** (6) 157 (1996).

26. Carre, B., and Pierre, C., *Proceedings of Tappi Papermakers Conference,* 16 (1993).

27. Ford, P., *Proceedings of Tappi Papermakers Conference,* 501 (1991).

28. Coates, P., *Proceedings of the 15th International Conference on Pulping and Papermaking*, 31 (1991).

29. Wägberg, L., and Lindström, T., *Nordic Pulp Paper Res. J.*, **2**, 49 (1982).

30. Krogerus, B., *Nordic Pulp Paper Res. J.*, **8,** (1), 135 (1993).

31. Carlson, U., *Proceedings of XXIV EUCEPA Conference*, 161 (1990).

32. Warnas, B., and Litchfield, T., *Svensk Papperstidning,* **15**, 18 (1987).

33. Allen, L., and Yaraskavitch, I., *Tappi J.*, **74**, (7), 79 (1991).

34. Honig, D., Harris, E., Pawlowska, L., O'Toole, M., and Jackson, L., *Pappi J.*, **76,** (9), 135 (1993).

35. Yu, X., and Somasundaran, P., *J. Colloid and Interface Sci.*, **177**, 283 (1996).

36. Ödberg, L., and Wägberg, L., *Papier,* **37** (10A), 43 (1989).

37. Ono, H., and Deng, Y., *Accepted to Present at Eleventh Fundamental Research Symposium*, London, September, 1997.

38. Goodwin, J., Ottewill, R., and Pelton, R., *Colloid Polym. Sci.*, **257**, 61 (1979).

39. Thomson, D., and Pownall, P., *J. Colloid and Interface Sci.*, **131**, 74 (1989).

40. Smallwood, P., *Colloid Polym. Sci.*, **255**, 881 (1997).

TABLE I. Microparticle preparations and the colloidal properties.

Sample	A	B	C	D	E
Styrene (mol)	0.108	0.108	0.108	0.108	0.108
MAPTAC (mol)	0	0	0.0019	0.0113	0.0338
C-surfactant (mol)	0	0.0089	0.0089	0.0089	0.0089
Water (L)	0.150	0.150	0.150	0.150	0.150
VA-044 (mol)	0.0007	0.0007	0.0007	0.0007	0.0007
DVB (mol)	0	0.0043	0.0043	0.0043	0.0043
Particle size (nm)	178.2	28.7	33.9	42.3	52.5
Polydispersity	0.17	0.17	0.24	0.41	0.34
Charge density ($\mu eq/m^2$)	-	2.84	3.04	3.58	2.91

Figure Captions

Figure 1. Zeta potentials of CPMP (sample A), PCC, and fibers as a function of pH. The zeta potential of fines was assumed to be representative of fibers.

Figure 2. Zeta potential and relative turbidity of 0.05% PCC suspension as a function of CPMP (sample D) concentration at pH 8.9.

Figure 3. Zeta potential and relative turbidity of PCC suspension as a function of poly-DADMAC concentration at pH 8.9 and 0.05 wt% PCC.

Figure 4. Zeta potential of PCC as a function of the concentrations of Na_2CO_3, $CaCl_2$, and APAM at pH 9.

Figure 5. Relative turbidity and zeta potential of PCC suspension in 0.47-mmol/L sodium carbonate as a function of CPMP (sample D) concentration.

Figure 6. Relative turbidity of PCC suspension as a function of chemical addition. A: PCC and CPMP in water; B: PCC and CPMP in 0.47 mmol/L Na_2CO_3 solution; C: CPMP was added into APAM-pretreated PCC; D: CPMP was added into PCC before adding APAM.

Figure 7. Relative turbidity as a function of CPMP concentration in washed and unwashed fibers.

Figure 8. First pass PCC retention on fiber web as a function of concentrations of 54 nm and 364 nm CPMPs. 1% original wood fibers and 20% PCC (based on dry fiber weight) were used.

Figure 9: Adsorption isotherms of CPMP on PCC surface. A: PCC in deionized water; B: APAM-pretreated PCC; C: PCC in 0.5-M Na_2CO_3 aqueous solution.

Figure 10. Zeta potential of PCC suspension as a function of equilibrium concentration of CPMP. A: PCC in deionized water; B: APAM-pretreated PCC; C: PCC in 0.5-M Na_2CO_3 aqueous solution.

Figure 11. The retention of APAM-pretreated PCC on washed fiber surface and the zeta potential of fines as a function of CPMP concentration.

Figure 12. The retention of APAM-pretreated PCC on washed fiber surface and zeta potential of fines as a function of APAM concentration in the presence of 40 mg/L CPMP.

Figure 13. Proposed flocculation mechanisms. A: PCC and CPMP in water; B: PCC and CPMP in Na_2CO_3 solution; C: CPMP was added into APAM-pretreated PCC; D: CPMP was added into PCC before adding APAM.

Figure 14. Flocculation by bridge formation between cationic patch and anionic water-soluble polymer. A: Most of the charges on cationic polymer are neutralized because the polymer flattened on negatively charged suspension surface. B: Only the charges that immediately attached to the negatively charged suspension surface are neutralized.

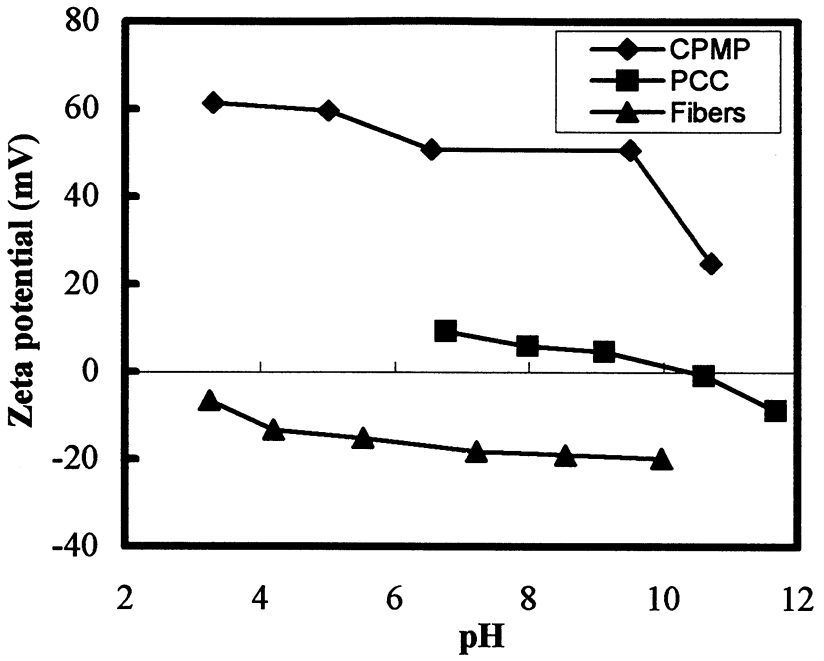

Figure 1. Zeta potentials of CPMP (sample A), PCC, and fibers as a function of pH. The zeta potential of fines was assumed to be representative of fibers.

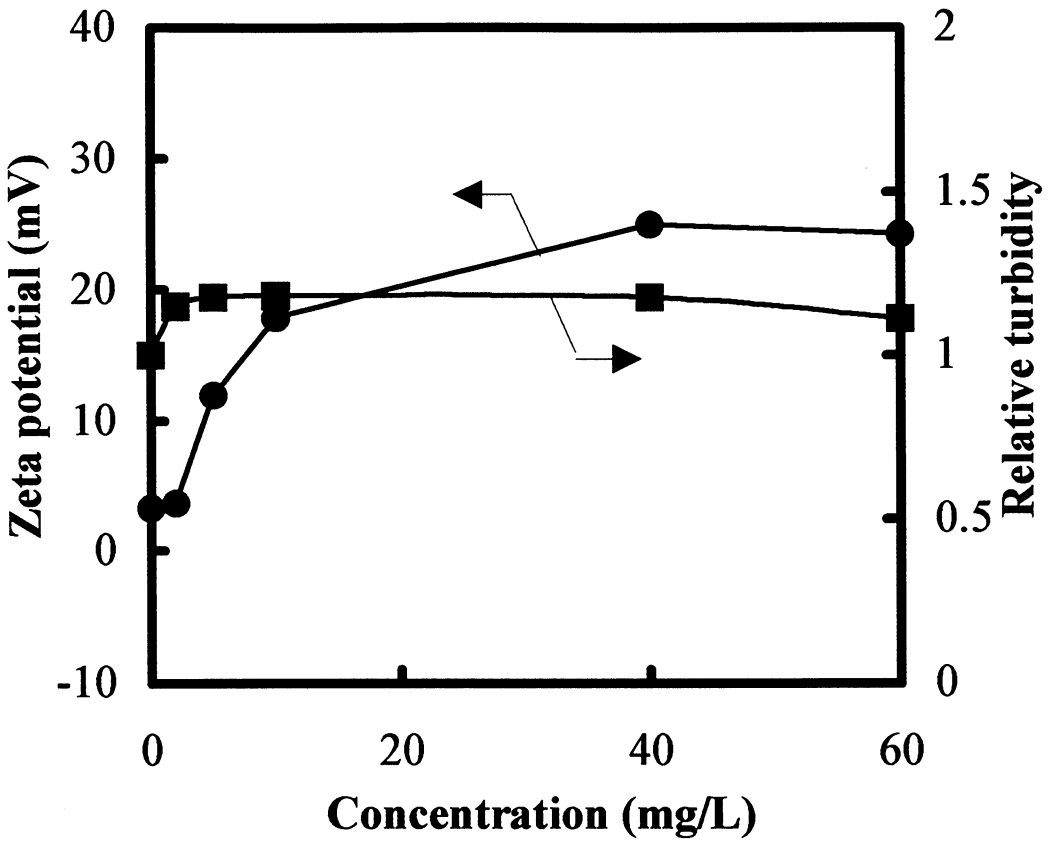

Figure 2. Zeta potential and relative turbidity of 0.05% PCC suspension as a function of CPMP (sample D) concentration at pH 8.9.

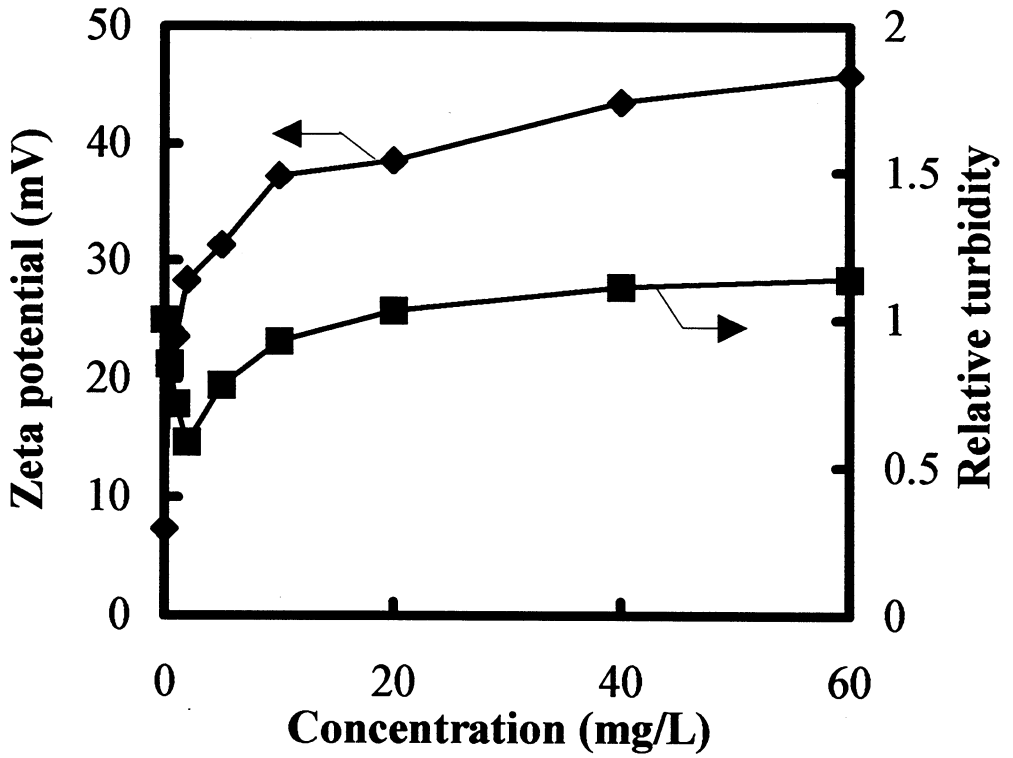

Figure 3. Zeta potential and relative turbidity of PCC suspension as a function of poly-DADMAC concentration at pH 8.9 and 0.05 wt% PCC.

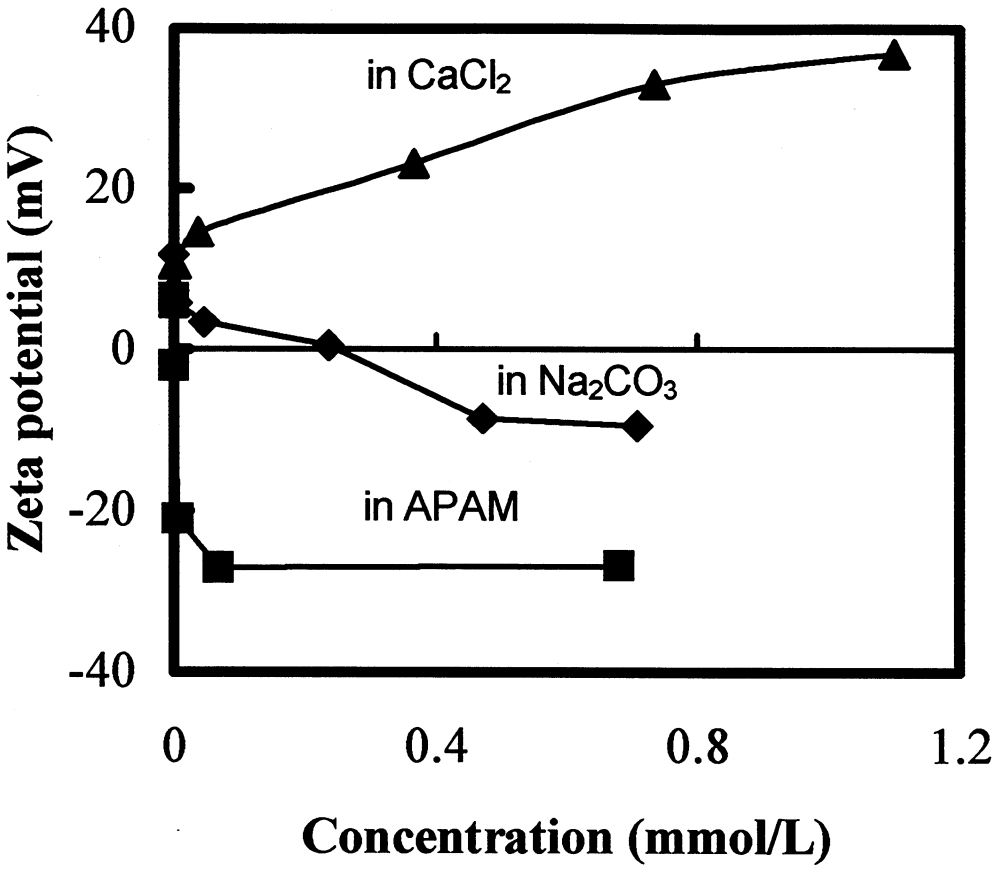

Figure 4. Zeta potential of PCC as a function of the concentrations of Na_2CO_3, $CaCl_2$, and APAM at pH 9.

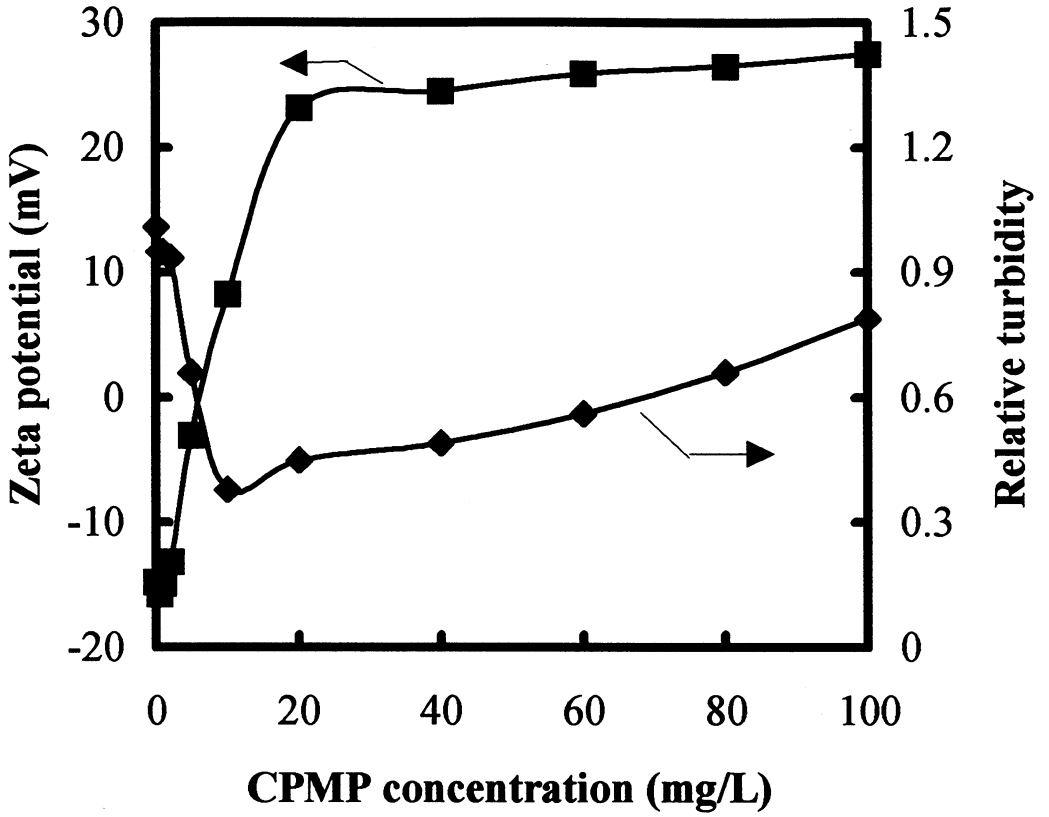

Figure 5. Relative turbidity and zeta potential of PCC suspension in 0.47 mmol/L sodium carbonate as a function of CPMP (sample D) concentration.

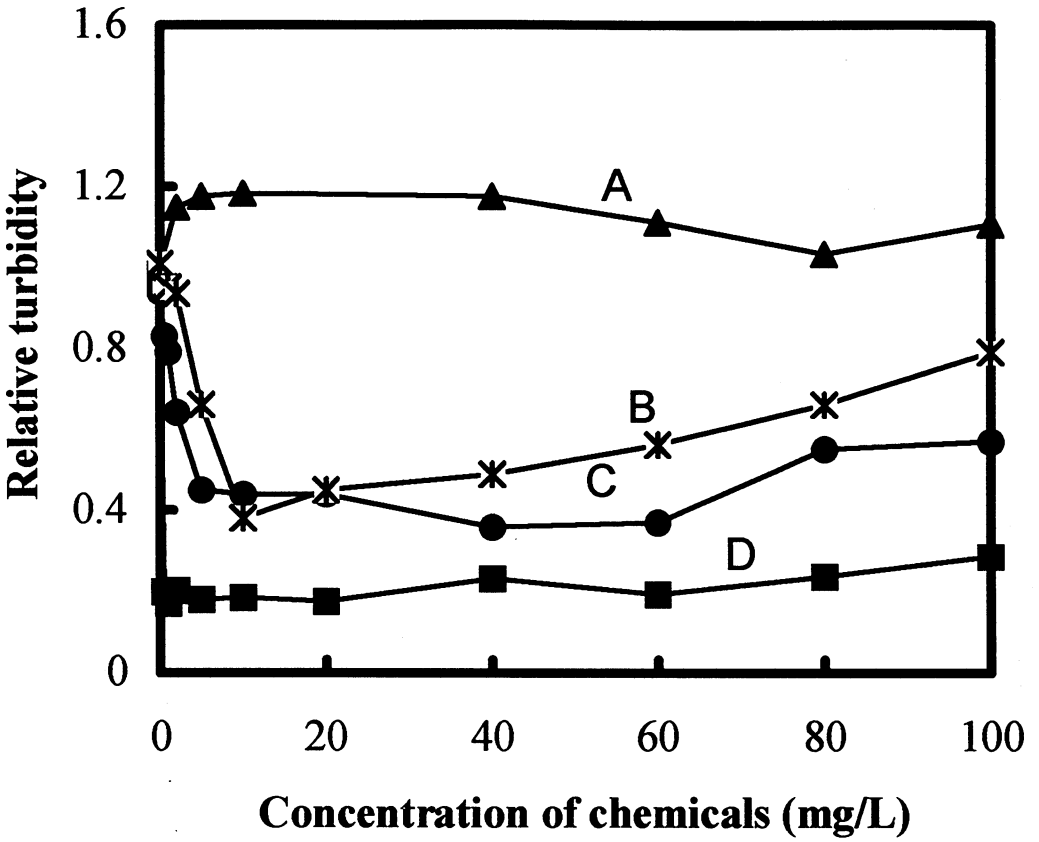

Figure 6. Relative turbidity of PCC suspension as a function of chemical addition. A: PCC and CPMP in water; B: PCC and CPMP in 0.47-mmol/L Na_2CO_3 solution; C: CPMP was added into APAM-pretreated PCC; D: CPMP was added into PCC before adding APAM.

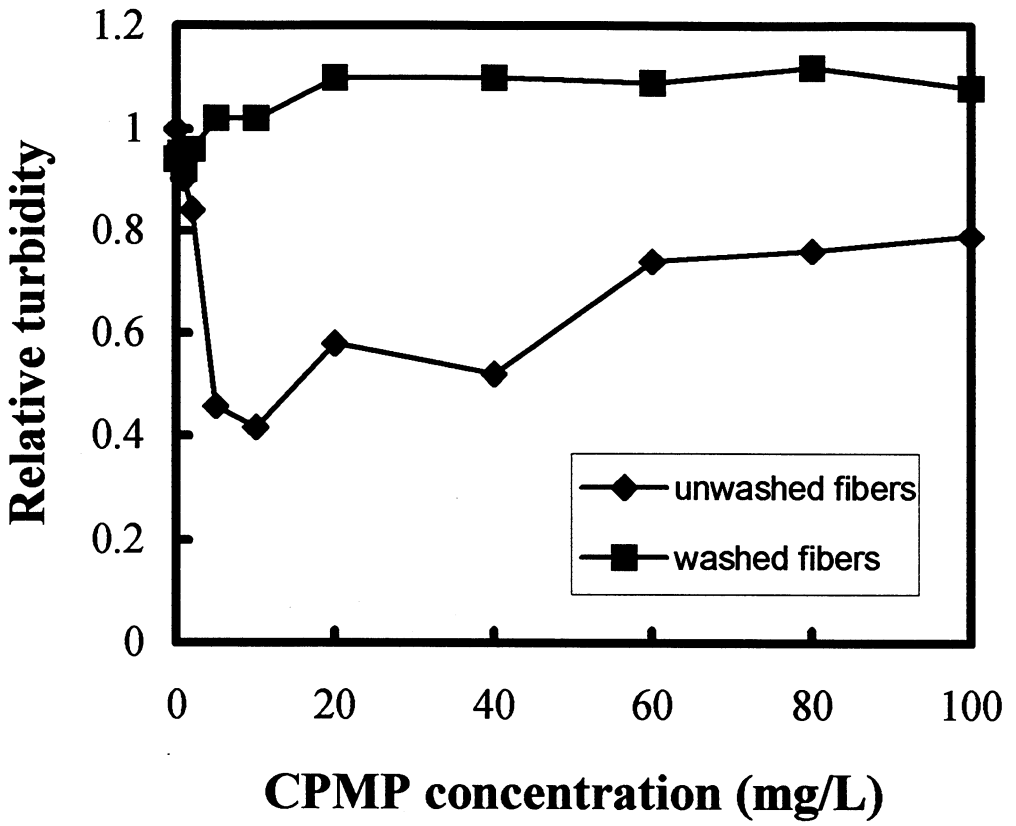

Figure 7. Relative turbidity as a function of CPMP concentration in washed and unwashed fibers.

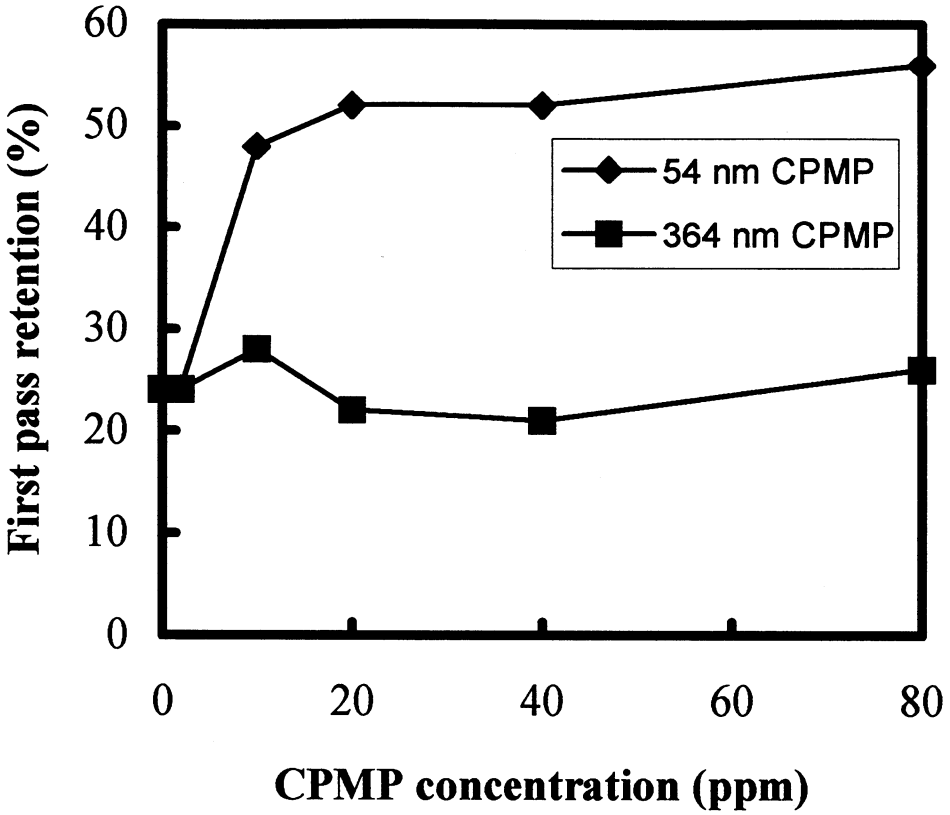

Figure 8. First pass PCC retention on fiber web as a function of concentrations of 54 nm and 364 nm CPMPs. 1% original wood fibers and 20% PCC (based on dry fiber weight) were used.

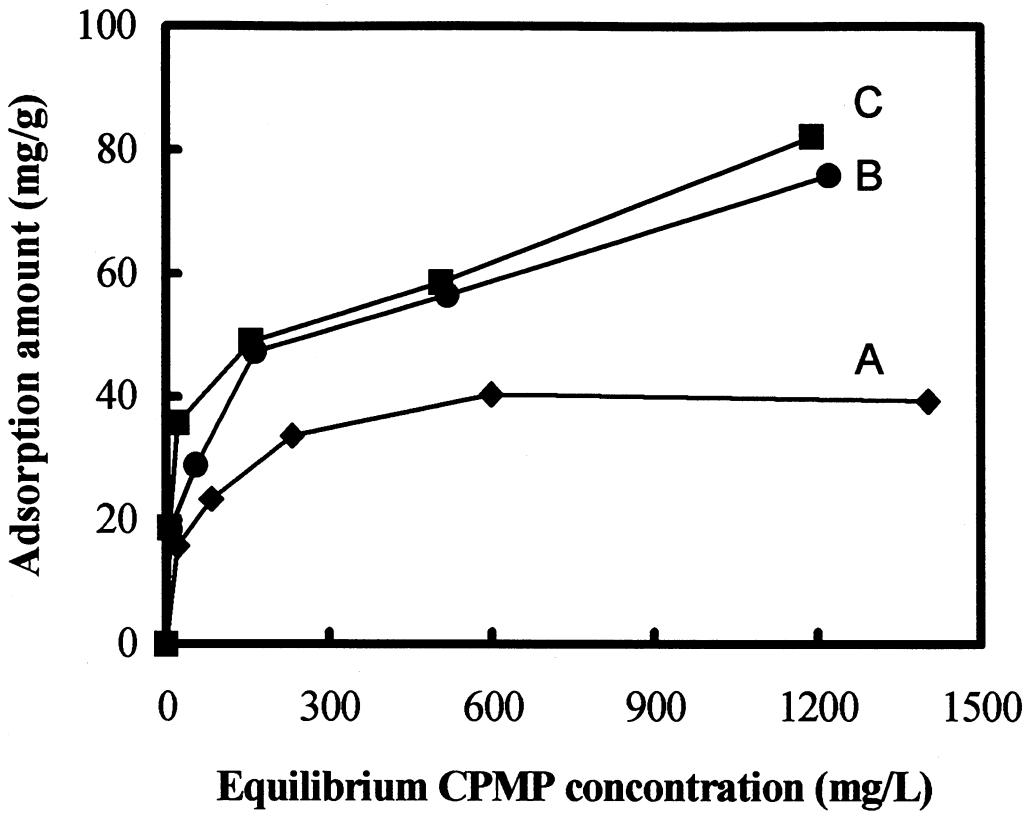

Figure 9: Adsorption isotherms of CPMP on PCC surface. A: PCC in deionized water; B: APAM-pretreated PCC; C: PCC in 0.5-M Na_2CO_3 aqueous solution.

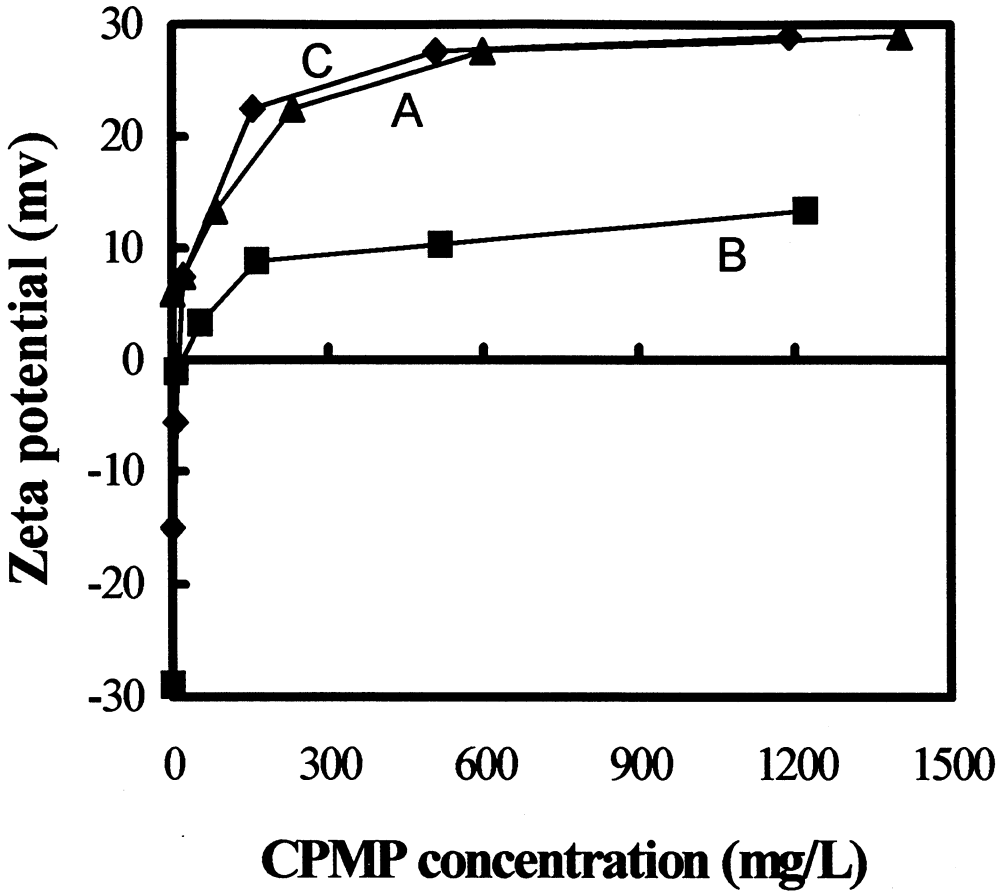

Figure 10. Zeta potential of PCC suspension as a function of equilibrium concentration of CPMP. A: PCC in deionized water; B: APAM-pretreated PCC; C: PCC in 0.5-M Na_2CO_3 aqueous solution.

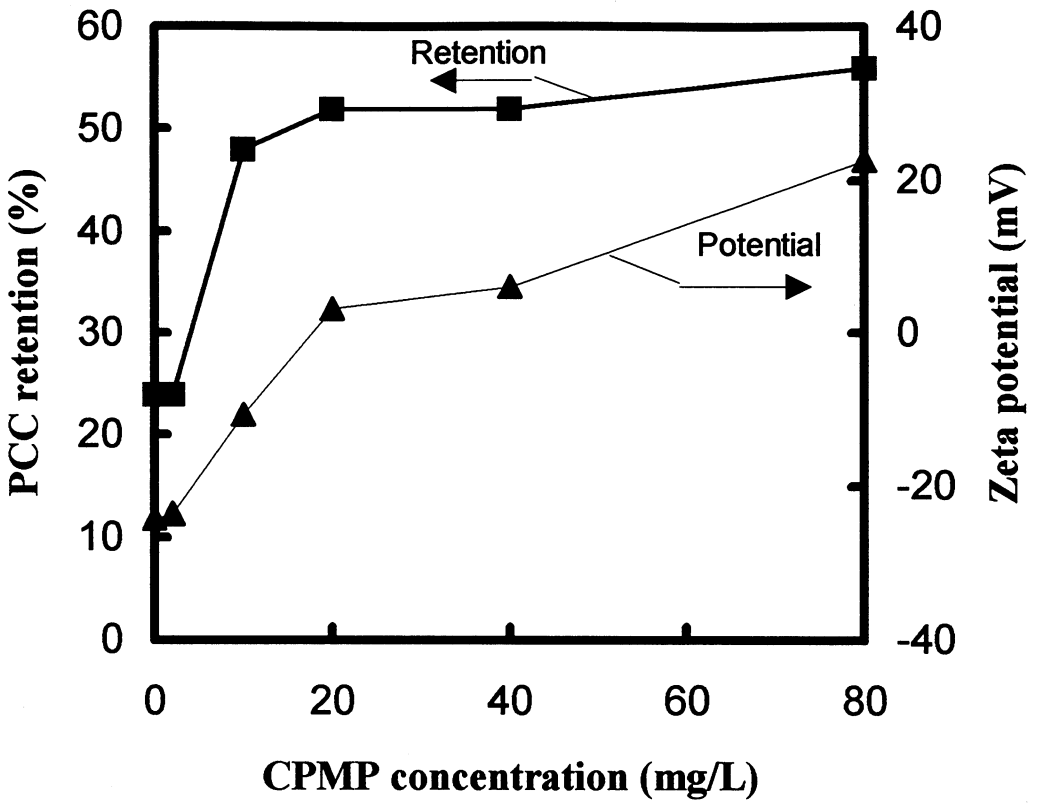

Figure 11. The retention of APAM-pretreated PCC on washed fiber surface and the zeta potential of fines as a function of CPMP concentration.

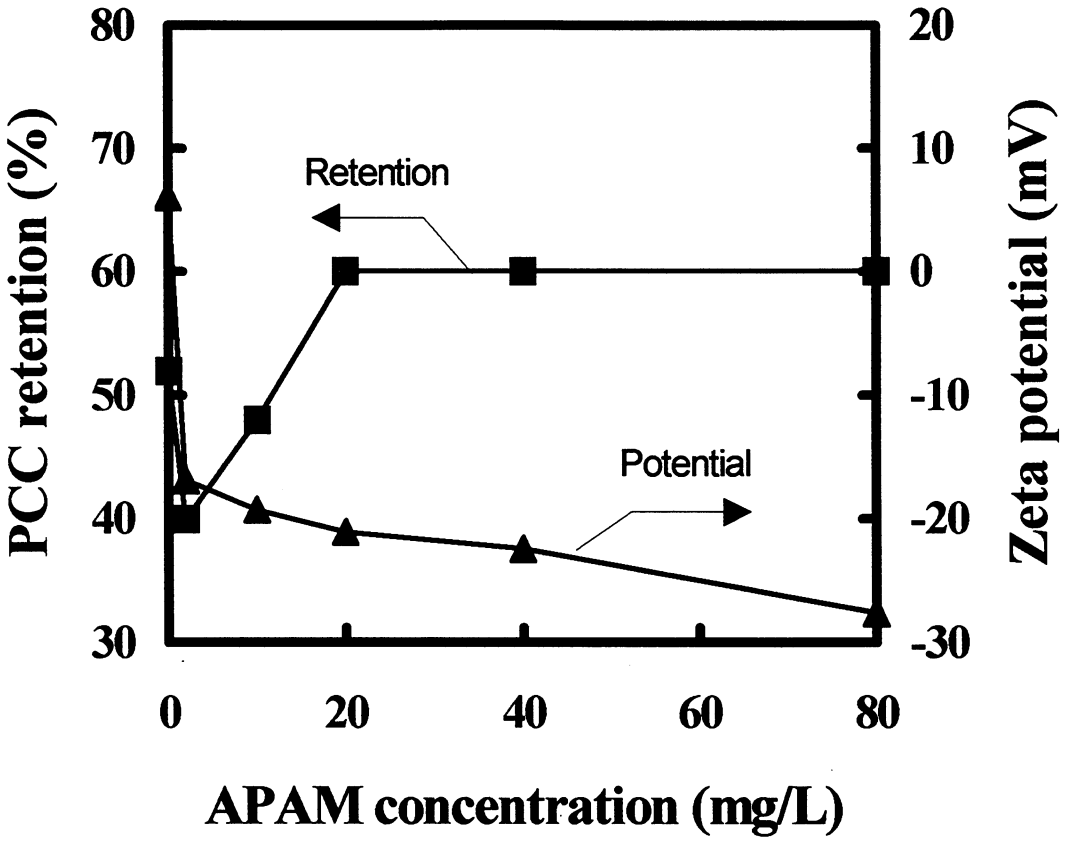

Figure 12. The retention of APAM-pretreated PCC on washed fiber surface in the presence of 40 mg/L CPMP and zeta potential of fines as a function of APAM concentration.

Figure 13-A:

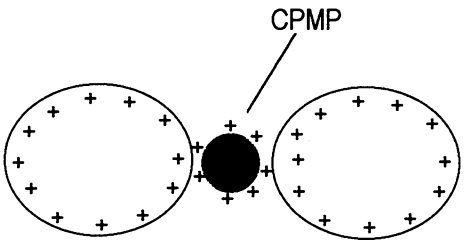

Figure 13-B:

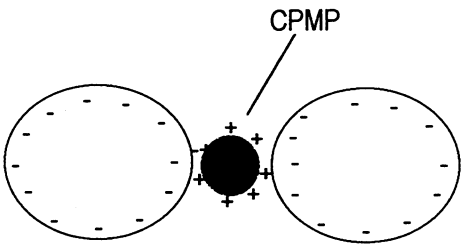

Figure 13-C:

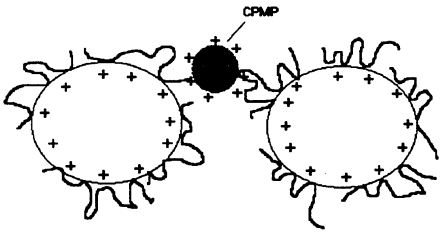

Figure 13-D:

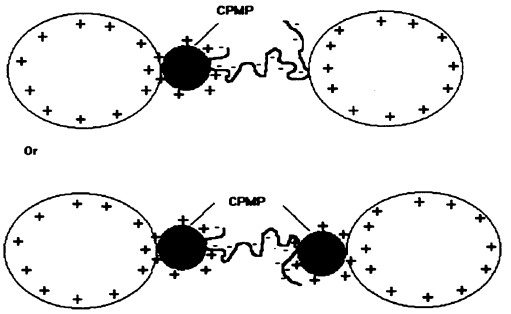

Figure 13. Proposed flocculation mechanisms. A: PCC and CPMP in water; B: PCC and CPMP in Na_2CO_3 solution; C: CPMP was added into APAM-pretreated PCC; D: CPMP was added into PCC before adding APAM.

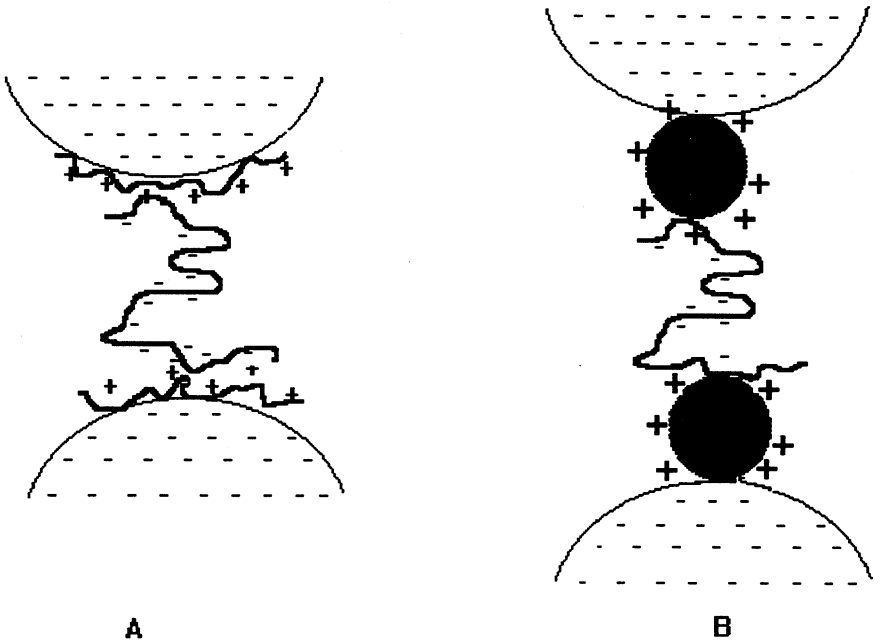

Figure 14. Flocculation by bridge formation between cationic patch and anionic water-soluble polymer. A: Most of the charges on cationic polymer are neutralized because the polymer flattened on negatively charged suspension surface. B: Only the charges that immediately attached to the negatively charged suspension surface are neutralized.